Sludge Incineration and Precipitant Recovery

Volume II

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**earch Program for the Abatement of Municipal Pollution
under Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality**

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RESEARCH REPORTS

These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Fisheries and Environment Canada, and the Ontario Ministry of Environment, and contracts with municipalities, research institutions and industrial organizations.

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Sludge incineration and
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/ Fowlie, P. J. A.

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SLUDGE INCINERATION AND PRECIPITANT RECOVERY

VOLUME II

by

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RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION UNDER THE
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ABSTRACT

In this study, multiple hearth incinerator ash produced from iron-rich primary sludge from a phosphorus removal process was leached at bench scale with various acids and alkalis to recover iron for recycle to the phosphorus removal process.

Sulphuric and hydrochloric acids produced good iron extractions. The optimum sulphuric acid concentration for leaching increased linearly with incineration temperature. For each temperature of ash there was an optimum acid concentration above which the solubility of iron decreased.

The optimum hydrochloric acid concentration for leaching showed little dependence on incineration temperature. Iron extraction increased with increasing acid concentration.

The recovery of the iron from the acid extracts in a usable form for phosphorus removal was also investigated at bench scale. The addition of concentrated sulphuric acid (98 wt%, 18 M) to the sulphuric acid leachate (31.4 vol%, 5.65 M) caused precipitation of ferric sulphate from the resultant solution (46 vol%, 8.3 M). This precipitate was then dissolved in water or effluent to give a solution usable for phosphorus removal from municipal sewage.

A preliminary cost evaluation of the iron recovery process was carried out. It showed that the ferric sulphate recovery costs were more than double the cost of commercial ferric chloride.

RÉSUMÉ

Les cendres riches en fer, provenant de l'incinération, dans un four à foyers multiples, de la boue d'un traitement primaire de déphosphatation ont été lixiviées en laboratoire, à l'aide de divers acides et alcalis. Le fer ainsi récupéré sert au procédé de déphosphatation.

Les acides chlorhydrique et sulfurique ont favorisé l'extraction du fer. La concentration optimale d'acide sulfurique nécessaire à la lixiviation augmente de façon linéaire avec la température d'incinération. A chaque température des cendres correspond une concentration optimale d'acide au-delà de laquelle le fer devient moins soluble.

La concentration optimale d'acide chlorhydrique, cependent, est très peu dépendante de la température d'incinération. Le taux d'extraction du fer a augmenté avec la concentration de l'acide.

Nos expériences en laboratoire ont aussi porté sur la récupération du fer des extraits acides, sous une forme utilisable pour la déphosphatation. L'addition d'acide sulfurique concentré (98 p. 100 en poids, 18M) au percolat d'acide sulfurique (31,4 p. 100 en vol., 5,65 M) fait précipiter le sulfate ferrique de la solution résultante (46 p. 100 en vol., 8,3 M). Ce précipité dissous par la suite dans l'eau ou dans l'effluent a produit une solution convenant à la déphosphatation des égouts municipaux.

Une première évaluation du coût de cette récupération du fer a démontré que le sulfate ferrique ainsi obtenu coûtait deux fois plus le chlorure ferrique du commerce.

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CONCLUSIONS

1. Iron can be leached from iron-rich incinerator ash using either sulphuric or hydrochloric acid.
2. Iron can be precipitated from a sulphuric acid leachate by the addition of concentrated sulphuric acid.
3. The resulting $Fe_2(SO_4)_3$ product can be used to remove phosphorus from municipal wastewater provided the wastewater has sufficient alkalinity to neutralize the excess sulphuric acid and has a neutral to alkaline pH. With low alkalinity wastewaters, lime must be added to neutralize the excess acid.
4. The cost of H_2SO_4 to recover Fe^{3+} was estimated at \$1.21/kg Fe^{3+} (56¢/lb Fe^{3+}). This was higher than the cost of commercial ferric chloride [53¢/kg Fe^{3+} (24¢/lb Fe^{3+})].

1 BACKGROUND AND STUDY OBJECTIVES

1.1 Background

The incineration of sewage sludge has increased in urban centres where land for the ultimate disposal of sewage sludge is restricted or is too distant to be used economically. Requirements for phosphorus removal from municipal wastewater treatment effluents have caused an increase in sludge volumes with considerably higher concentrations of phosphorus, its associated precipitant metals (e.g., Fe^{3+}, Al^{3+}, Ca^{2+}), and other co-precipitated metals which normally accumulate in the sludges. These elements survive the incineration process and appear in the incinerator ash. They will increase the weight of ash to be disposed of and may also cause long term environmental problems due to metal leaching from ash disposal sites.

These problems may possibly be alleviated by recovering the precipitant and recycling it within the treatment plant for phosphorus removal. Recovery costs may be partially offset by the lower quantity of fresh precipitant chemical that would be required. Shannon et al (1974) have indicated that such recovery may be feasible.

Any scheme for recovering iron must involve selective solubilization of the iron, or solubilization of several other components, followed by their separation. In practice, a combination of both appears to be most feasible. The most important separation must be iron from phosphorus since, without this separation, recycle of the precipitant would result in little, if any, phosphorus removal. Other metals (Al, Cr, Cu, Ni, Zn) common in sewage tend to react similarly to iron. If they are recycled with the precipitant, they tend to accumulate in the treatment system and eventually appear in the effluent. Adverse effects on biological processes may also result. These metals must be separated from the recycled iron.

Processes for precipitant recovery generally involve the use of acids or alkalis. The final product to be recycled to the plant should not contain a large excess of acids or alkalis as they will disrupt plant operation by causing a pH shift away from the optimum range for phosphorus removal and/or biological treatment. Since iron salts are relatively cheap as bulk commodities, efficient use of chemicals in the recovery process is mandatory if it is to be economical.

Diosady (1974) studied the ash (3% to 5% Fe) from the Ashbridges Bay sewage treatment plant incinerator in Toronto and determined that $73.00 per ton ash could be realized by chemical recovery of Cr, Cu, Ni, Pb, Zn and P. He was unable to recover iron from this ash, but was able to separate it from the previously mentioned components by dissolving the ash in 60 wt%, H_2SO_4(11 M), separating the metals by cation exchange and removing the phosphoric acid by vacuum distillation. The remaining sulphuric acid could be recycled. The iron, in this case, remained in the undissolved portion of ash. He also determined that iron would dissolve in sulphuric acid at concentrations less than 60 wt%. Hydrochloric and phosphoric acids were also good solvents for iron.

Scott (1973) tested ash from the same source along with other waste products for iron recovery using sulphuric acid. Using 3.9 wt% H_2SO_4 (0.7 M) at 76°C, only 30% dissolution of iron from the ash was achieved in three hours.

Oliver and Carey (1976) found that iron, phosphorus and other metals in incinerator ashes could be effectively dissolved in 60 wt% H_2SO_4. Dissolution required 225 L (50 Igal) of 98% H_2SO_4 (18 M) per 909 kg (ton) ash. The addition of NH_4OH and $(NH_4)_2SO_4$ to pH 9 to 10 resulted in an iron hydroxide precipitate and a solution containing the other components.

Scott and Horlings (1974) studied the removal of metals and phosphorus from sewage sludges. Metals could be leached from the sludge by using a small excess of sulphuric acid. They then separated Al, Fe, Cr, Cu, Zn and P by selective precipitation at controlled pH using NaOH or $Ca(OH)_2$. Although this recovery and separation scheme appears viable and economical for the sludges studied, the high acid concentration necessary to leach incinerator ash would render the process uneconomical since considerably larger quantities of sulphuric acid must subsequently be neutralized. These authors also tested a liquid ion exchange process which uses triphenyl tin hydroxide to extract phosphate ion from the acid solution. This met with little success. They also suggested using tertiary amines or tri-n-butyl phosphate for selective extraction of iron.

Herbert (1966), Criss and Olsen (1968) and Gray and Penessis (1972) reported chemical analyses of incinerator ashes from various cities in the United States. The results are presented in Table 1, along with ash data from the Hamilton and Toronto Ashbridges Bay sewage treatment plants obtained in this study. The main constituents of the ash are silicon, aluminum, iron, calcium and phosphorus.

TABLE 1. AVERAGE COMPOSITION OF INCINERATOR ASHES

Constituent*	Herbert (1966)	Criss & Olsen (1968)	Gray & Penessis (1972)	Hamilton, Ont. (1974)	Toronto, Ont. (1974)
Al_2O_3	18.35	17.44	12.0	5.7	13.2
CaO	9.94	10.52	27.0	14.0	14.0
CuO	**	trace	**	0.4	0.4
Fe_2O_3	8.85	9.26	10.3	21.4	4.3
Na_2O	3.25	6.09	0.35	**	**
K_2O	1.36	1.99	0.22	0.4	0.2
MgO	2.54	2.1	1.9	3.3	0.8
MnO_2	**	.29	**	**	**
NiO	**	**	**	0.13	0.04
PbO	**	trace	**	0.4	0.3
SiO_2	46.3	44.73	29.3	37.8	37.8
ZnO	1.37	1.54	**	2.5	1.0
PO_4	2.83	2.00	10.8	15.0	4.5
SO_4	1.15	4.42	3.2	**	**

*all values expressed in percent
**no analysis reported

1.2 Study Objectives

The objectives of this study were:

1. to investigate at laboratory scale the leaching characteristics of high iron content incinerator ashes such as would result from a sewage treatment plant using iron salts for phosphorus removal;

2. to determine the required unit operations and design data to recover an iron salt from such an ash;
3. to evaluate the economics of such an iron recovery process; and
4. to assess the effectiveness of the recovered iron salt as a precipitant for phosphorus removal.

2 EXPERIMENTAL PROCEDURES

2.1 Procedures Used to Investigate the Leaching Characteristics of the Ash

The Hamilton sewage treatment plant does not have a conventional phosphorus removal system but has a sufficiently high influent iron concentration to give good phosphorus removal. Vacuum filtered sludge from this plant was burned at temperatures of 760°C (1400°F), 816°C (1500°F), 871°C (1600°F) and 927°C (1700°F) at a one-hour residence time in a multiple hearth incinerator (Plummer, 1975). The incinerator ash contains about 15 wt% iron and 5 wt% phosphorus. The ashes were tested for iron recovery using sulphuric acid, hydrochloric acid, nitric acid, sodium hydroxide, calcium hydroxide, and ammonium hydroxide plus ammonium sulfate.

The experimental equipment used is shown in Figure 1 and consists of a constant temperature water bath with four, one-litre Erlenmeyer flasks each with motor and teflon paddle. Two hundred and three hundred g/L ash solutions were examined. The variables studied were incineration temperature, time of leaching, leach solution (H_2SO_4, HCl, etc.), solution concentration and particle size of the ash.

Thirty to fifty cubic centimeters of stirred slurry were taken for analysis periodically with a polypropylene syringe. These were filtered hot through a 100-micron glass fibre filter for the determination of acid/alkali, soluble metals and soluble phosphorus.

2.2 Procedures Used to Investigate the Recovery of the Iron Salt

The same equipment (Figure 1) was used to test the precipitation of iron from the acid extract. The variables studied were precipitation temperature, time, acid concentration and initial precipitate (seed) concentration.

2.3 Procedures Used to Assess the Phosphorus Removal Performance of the Recovered Iron Salt

The phosphorus removal capability of the recovered iron salt was assessed using standard jar testing procedures as follows:

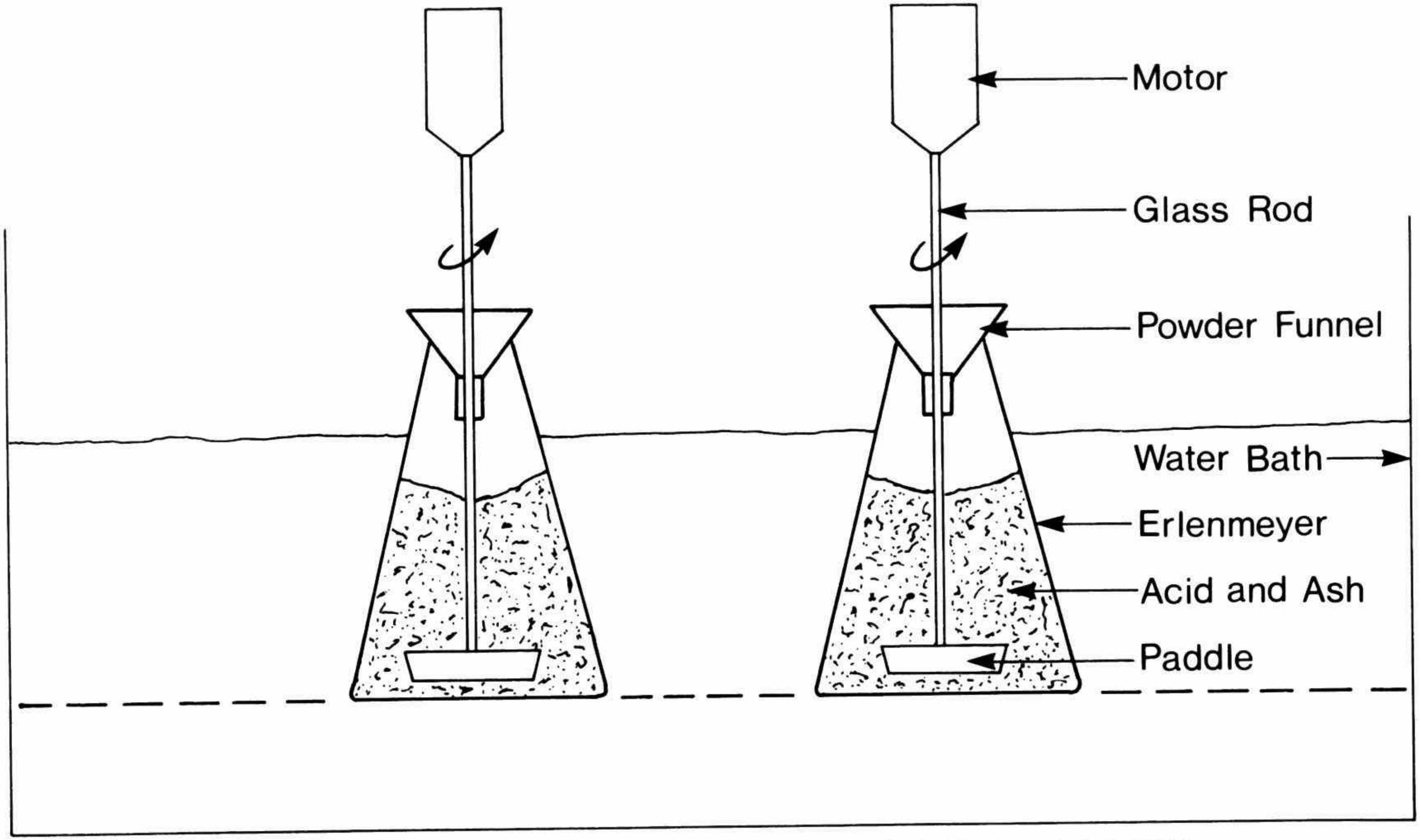
Motor
Glass Rod
Powder Funnel
Water Bath
Erlenmeyer
Acid and Ash
Paddle

FIGURE 1 EQUIPMENT USED IN THE IRON RECOVERY STUDIES

1. a 20-litre grab sample of raw degritted sewage was taken from the Burlington Skyway sewage treatment plant, and from it were taken 12, one-litre portions;
2. a quantity of commercial ferric chloride solution or recovered ferric sulfate solution was added to give concentrations ranging from 0 to 45 mg/L Fe^{3+};
3. the samples were placed on a Phipps and Bird six place stirrer and flash mixed five minutes at 100 rpm, flocculated 10 minutes at 40 rpm, settled 60 minutes at 10 rpm, and quiescently settled 10 minutes; and
4. a supernate sample was decanted for total phosphorus and/or metals analyses.

2.4 Analytical Methods

Iron was determined by the stannous chloride reduction/potassium dichromate titration method using barium diphenylaminesulfonate as the indicator according to Vogel (1960).

Other heavy metal samples were acid digested and analysed by atomic absorption spectrophotometry according to the methods of Traversy (1971).

Phosphorus was determined by the Technicon automated molyldenum blue method.

Free acid was determined by titrating with standard $NaHCO_3$ to pH 4.2 using a Fisher Accumet pH meter.

3 RESULTS AND DISCUSSION

3.1 Incinerator Ash Leaching

3.1.1 Ash leaching with sulphuric acid

Ash produced at 760°C (1400°F) in the multiple hearth incinerator from Hamilton sewage treatment plant vacuum filtered sludge was leached at 48°C (118°F), 69°C (156°F) and 90°C (194°F) using 15 vol% and 30 vol% sulphuric acid. The effect of leaching temperature on iron extraction is presented in Figure 2, and shows that increasing the extraction temperature increases the solubilization of iron from the ash.

Experiments with sulphuric acid for ash leaching were carried out on an ash sample from each of the four incineration temperatures: 760°C (1400°F), 816°C (1500°F), 871°C (1600°F) and 927°C (1700°F). The sulphuric acid concentration was varied from 5 vol% to 50 vol% (0.9 M to 9 M). Figure 3 shows a typical extraction curve for the 760°C (1400°F) product leached at 90°C (194°F) for various leaching times. The optimum sulphuric acid concentration for this ash sample appears to be at 15 vol%.

Further experiments were carried out with ash produced at higher incineration temperatures. The effect of incineration temperature on iron extraction is summarized in Figure 4. As the incineration temperature increases, there is a linear increase in the optimum sulphuric acid concentration for leaching. However, the extraction efficiency decreases as incineration temperature is increased, thus more acid will be consumed per unit iron dissolved. Higher incineration temperatures result in a more refractory ash which is more difficult to leach. Iron recovery is thus facilitated by burning the sludge at low temperatures. According to Plummer (1975), the lower temperature limit for good sewage sludge incineration is 1500°F to 1600°F (816°C to 871°C) for dewatered sludges tested. Salib (1975) made a similar observation but noted poor or incomplete combustion at lower temperatures.

The quantity and percent extraction of iron, phosphorus and six other metals in H_2SO_4 are presented in Table 2. In these tests, 200 grams of ash per liter acid was leached at 90°C (194°F) for four hours using the

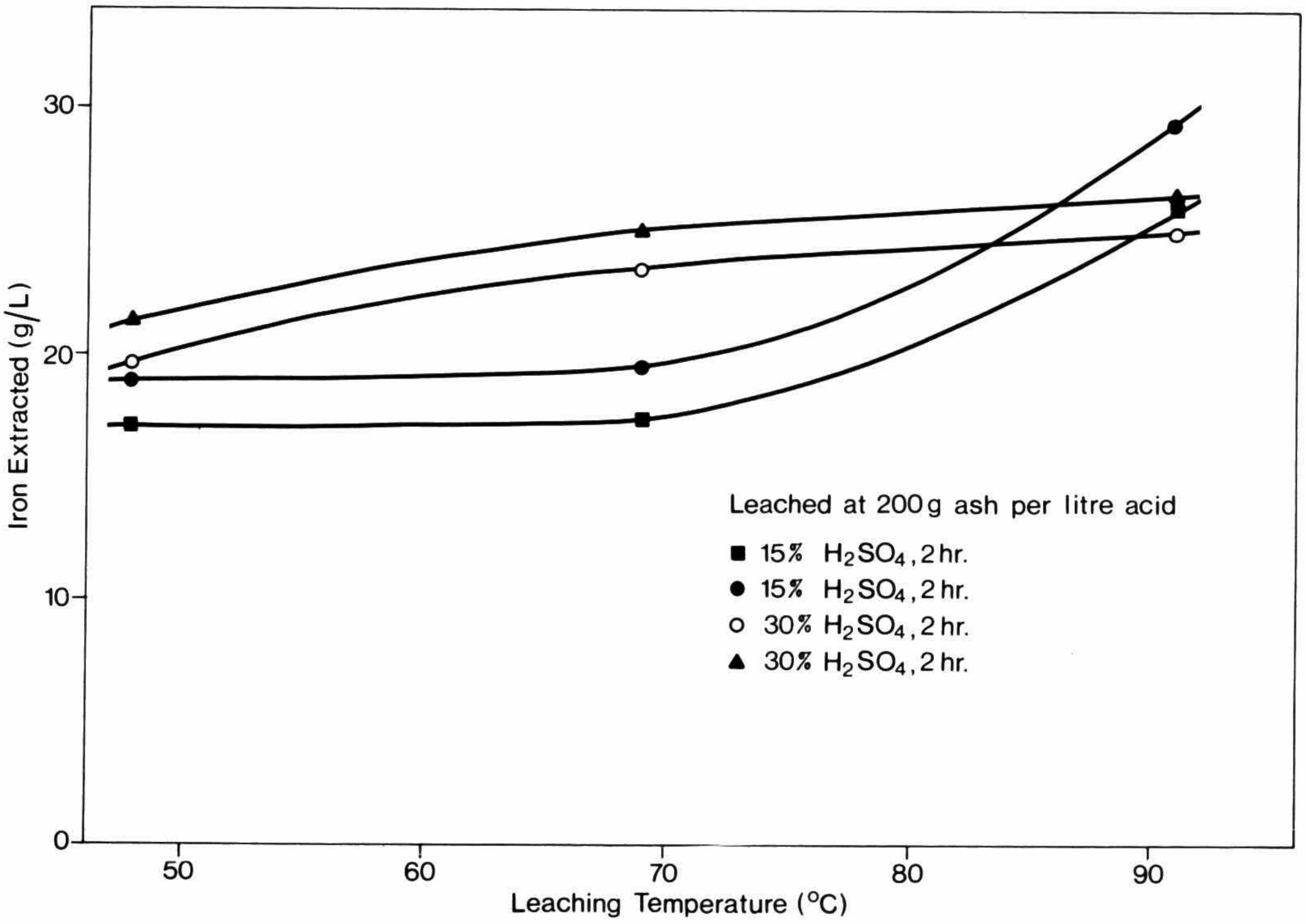

FIGURE 2 THE EFFECT OF SULPHURIC ACID LEACHING TEMPERATURE ON IRON EXTRACTION FROM 760 °C INCINERATOR ASH.

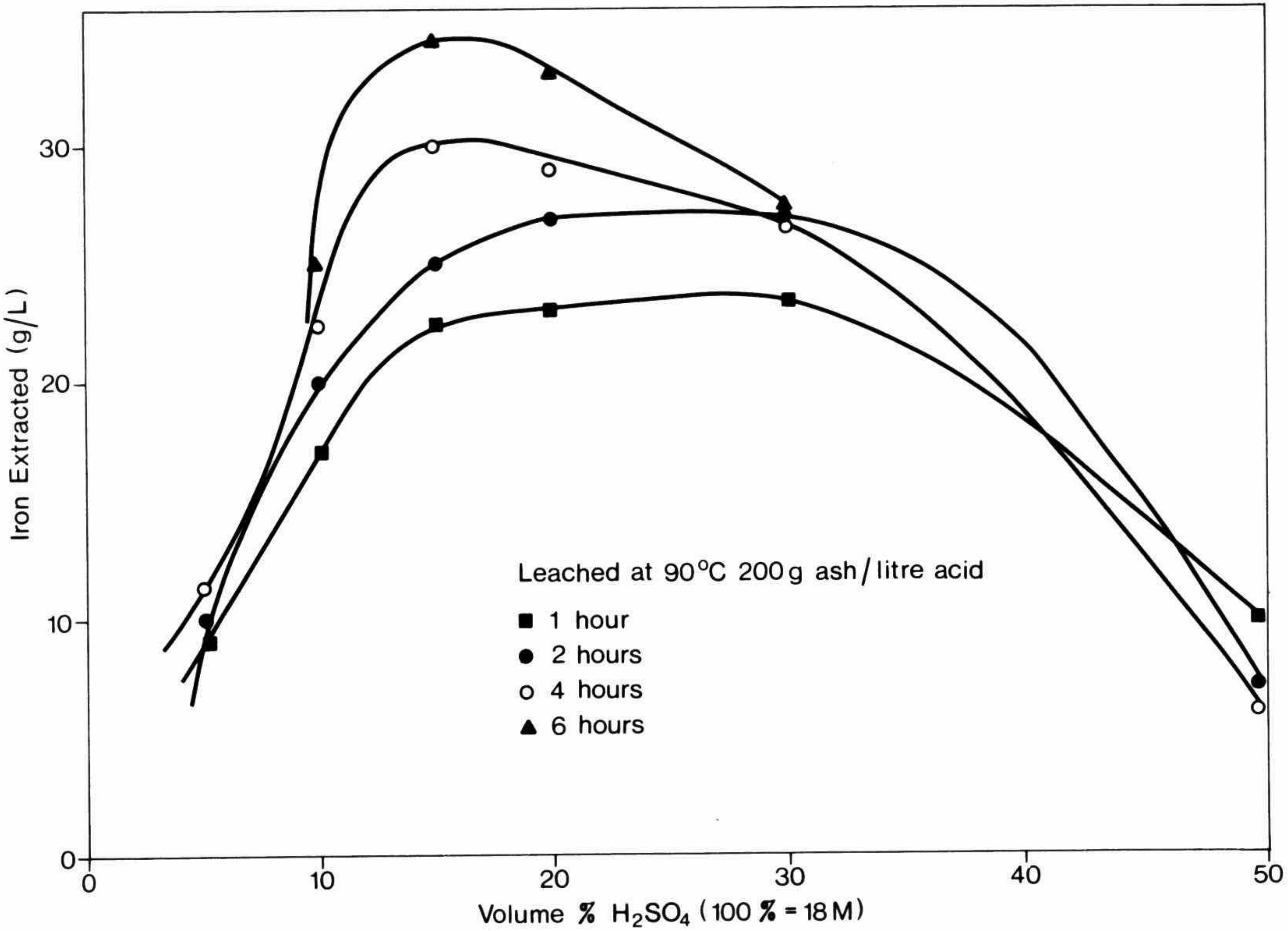

FIGURE 3 THE EFFECT OF SULPHURIC ACID CONCENTRATION AND LEACHING TIME ON IRON EXTRACTION FROM 760°C INCINERATOR ASH.

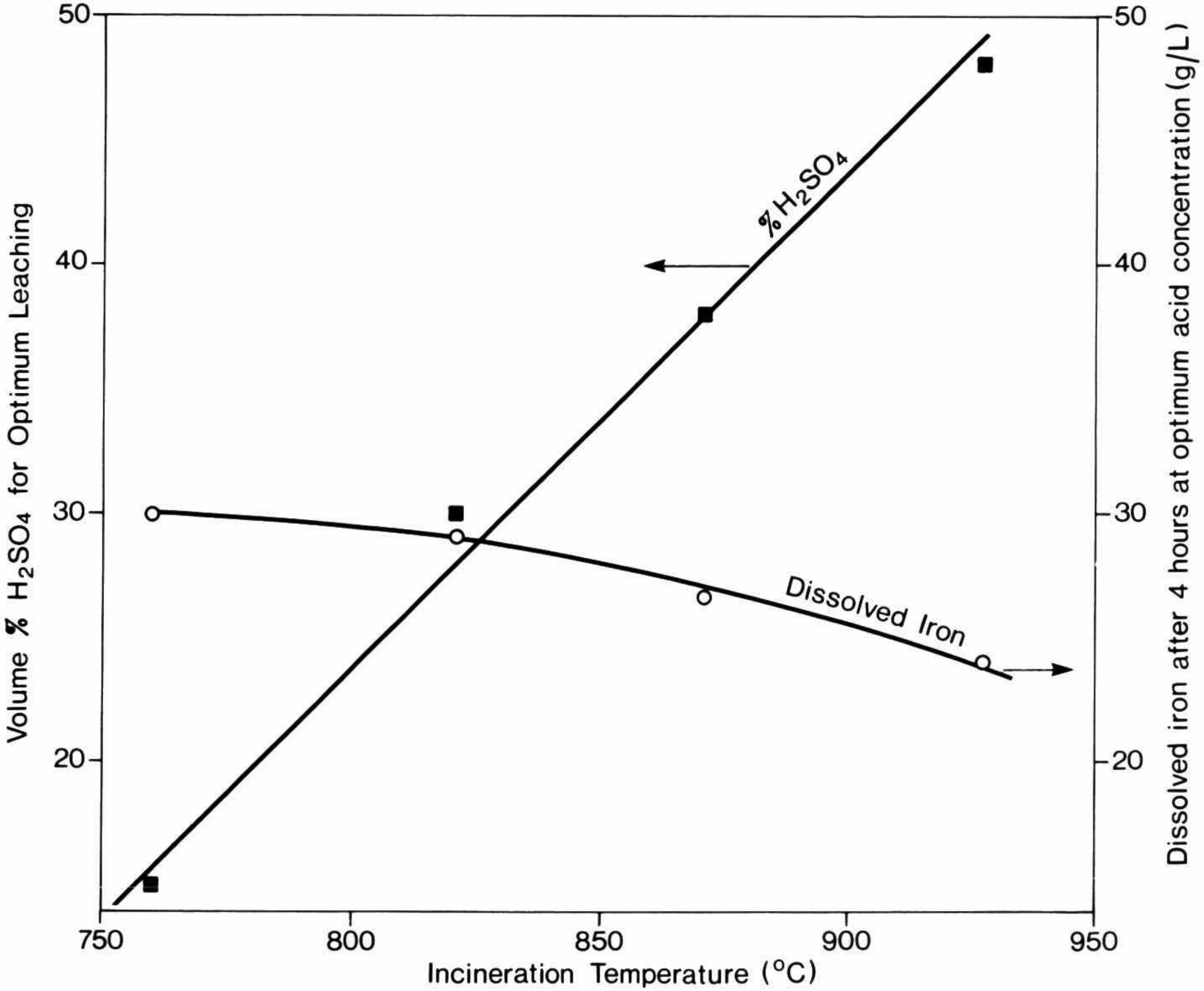

FIGURE 4 THE EFFECT OF INCINERATION TEMPERATURE ON SULPHURIC ACID LEACHING OF IRON FROM INCINERATOR ASH.

optimum H_2SO_4 concentration for each ash temperature (Figure 4). It should be noted that in some cases the reported percent extraction was greater than 100% because of analytical problems encountered with these incinerated ash samples (Diosady, 1974). Although an absolute analysis of the ash was difficult, trends in the ash composition and extraction efficiencies were obtained. [Approximately 100% of the iron was extracted from ashes incinerated at temperatures of 760°C (1400°F) and 816°C (1500°F)]. Ca and Pb are not soluble, while Al is only slightly soluble in sulphuric acid. Cu and P were nearly 100% extracted from all ash samples. Ni and Zn extractions varied with incineration temperature but a large portion could be extracted at their optimum temperatures.

TABLE 2. SULPHURIC ACID EXTRACTION EFFICIENCY OF ASH COMPONENTS*

	Fe	Al	Ca	Cu	Ni	Pb	Zn	P
% in ash (760°C)	13.1	2.38	9.16	0.261	0.062	0.162	1.44	4.8
Conc. in Extract (g/L)	29.4	3.10		0.570	0.052	0.002	3.38	10.0
% extracted	115	65	-	109	42	0.6	117	104
% in ash (816°C)	13.8	2.96	8.94	0.271	0.062	0.122	1.35	4.8
Conc. in Extract (g/L)	29.0	3.45	0.125	0.546	0.062	0.004	3.00	10.1
% extracted	105	58	0.7	101	50	1.6	111	105
% in ash (871°C)	14.1	3.10	8.88	0.250	0.058	0.066	1.11	4.9
Conc. in Extract (g/L)	26.5	2.83	0.160	0.486	0.108	0.0005	1.60	9.9
% extracted	94	46	0.9	97	93	0.4	72	101
% in ash (927°C)	14.1	2.70	7.54	0.277	0.049	0.098	1.27	5.1
Conc. in Extract (g/L)	24.0	3.80	0.300	0.544	0.098	0.005	2.02	9.7
% extracted	85	70	2	98	100	0.3	80	95

*Hamilton sewage treatment plant incinerated sludge.

Note: 200 grams of ash per litre of acid were leached at 90°C for four hours using the optimum H_2SO_4 concentration for each ash sample (i.e., 15 vol% H_2SO_4 at 760°C; higher for higher incineration temperatures according to Figure 4).

3.1.2 Ash leaching with hydrochloric acid

Samples of ash produced at 816^{0}C (1500^{0}F), 871^{0}C (1600^{0}F) and 927^{0}C (1700^{0}F) were leached at 90^{0}C (194^{0}F) in various concentrations of hydrochloric acid. A typical leaching curve for the 871^{0}C (1600^{0}F) ash is shown in Figure 5. The quantity of iron extracted increased with increasing acid concentration and did not exhibit a maximum as in the sulphuric acid case (Figure 3). Leaching with HCl was much quicker than with H_2SO_4. With an HCl concentration of 80 vol% (9.6 M), complete leaching was achieved in 20 minutes. At lower HCl concentrations somewhat lower dissolution occurred.

The quantity and percent extraction of iron, phosphorus and six other metals in HCl are presented in Table 3. In these tests, 200 grams ash per litre acid was leached at 90^{0}C (194^{0}F) for three hours using an 80 vol% HCl concentration.

TABLE 3. HYDROCHLORIC ACID EXTRACTION EFFICIENCY OF ASH COMPONENTS*

	Fe	Al	Ca	Cu	Ni	Pb	Zn	P
% in ash 816^{0}C	13.8	2.96	8.94	0.271	0.062	0.122	1.35	4.8
Conc. in extract (g/L)	26.0	3.57	17.0	0.527	0.129	0.530	2.83	10.2
% extracted	94	60	95	97	104	217	105	106
% in ash 871^{0}C	14.1	3.10	8.88	0.250	0.058	0.066	1.11	4.9
Conc. in extract (g/L)	27.5	2.46	18.0	0.550	0.138	0.330	2.42	9.8
% extracted	98	40	101	110	119	250	109	100
% in ash 927^{0}C	14.1	2.70	7.54	0.277	0.049	0.098	1.27	5.1
Conc. in extract (g/L)	29.0	2.80	16.0	0.522	0.104	0.272	1.92	9.8
% extracted	103	52	106	94	106	139	76	96

*Hamilton, Ontario, incinerated sludge.

Note: 20 grams of ash per litre of acid were leached at 90^{0}C (194^{0}F) for three hours using an 80 vol% HCl concentration.

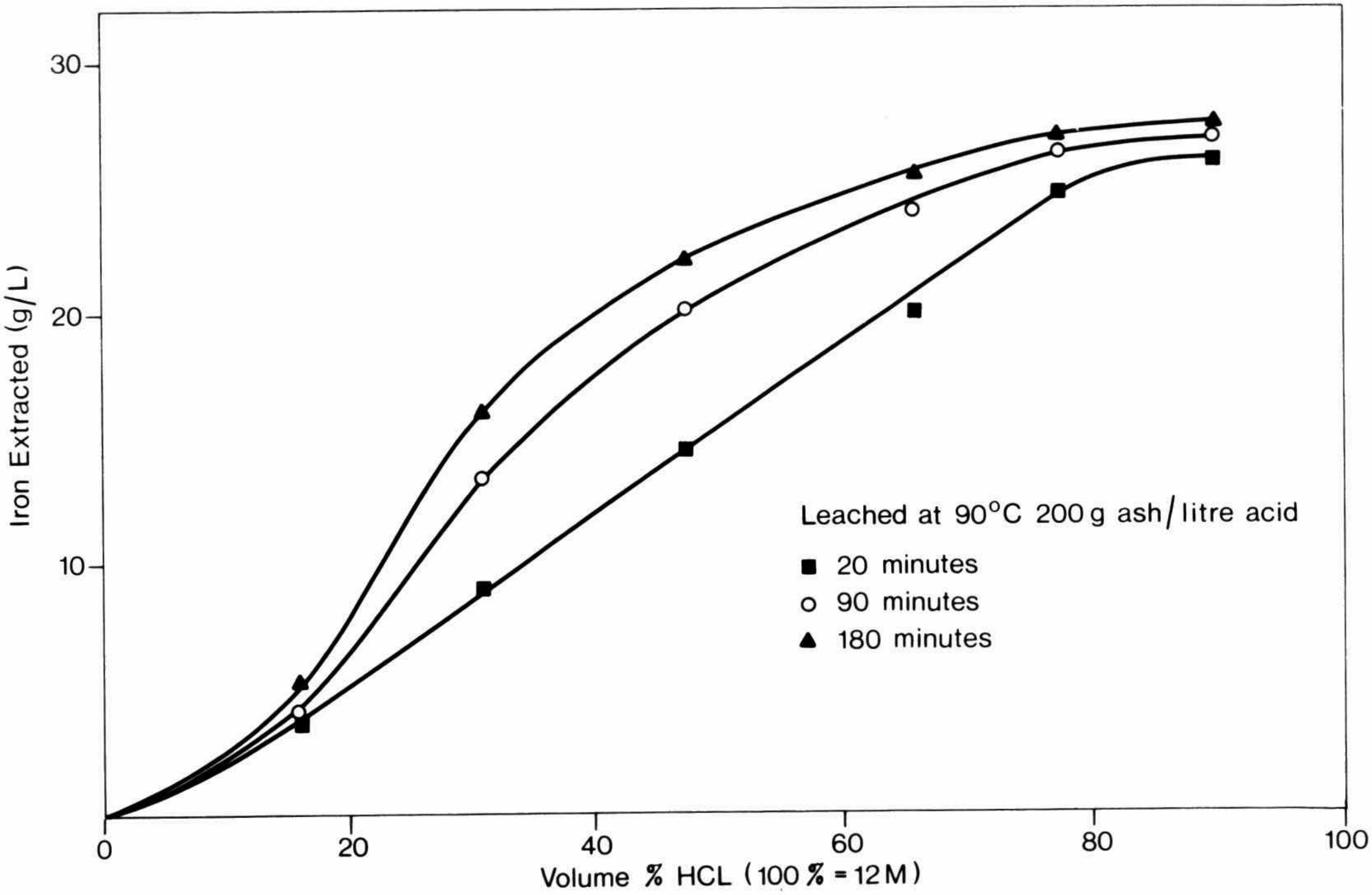

FIGURE 5 THE EFFECT OF HYDROCHLORIC ACID CONCENTRATION AND LEACHING TIME ON IRON EXTRACTION FROM 871°C INCINERATOR ASH.

The maximum iron concentration achieved was 26 g/L to 29 g/L as Fe^{3+}.

Phosphorus and all of the other metals, except aluminum which was 40% to 60% extracted, dissolved completely. Because of the aforementioned analytical difficulties (Diosady, 1974) much more lead appeared than was expected from the ash analysis.

3.1.3 Ash leaching with nitric acid

Nitric acid leaching of incinerator ash was attempted at 90°C (194°F) using HNO_3 concentrations varying from 20 vol% to 90 vol% HNO_3. The optimum concentration was determined to be 50 vol% acid. However, only 32% to 35% of the iron was recovered in three hours. Similar results were obtained by Diosady, 1974.

3.1.4 Ash leaching with mixtures of sulphuric and hydrochloric acid

Mixtures of HCl and H_2SO_4 were examined. For ashes produced at 871°C (1600°F) using sulphuric acid alone, the optimum acid concentration for leaching was found to be 38 vol% [6.8 M (Figure 4)]. With this total acid concentration, the ratio of $[HCl]/[H_2SO_4]$ was varied. The optimum ratio for iron leaching occurred at $[HCl]/[H_2SO_4]$ mole ratio of 0.277. Using this $[HCl]/[H_2SO_4]$ ratio, the total acid concentration was varied. The optimum for iron leaching occurred at 8 M total acid. This corresponds to 29 vol% HCl (3.5 M) plus 35 vol% H_2SO_4 (6.3 M), which is very close to the optimum acid concentration for sulphuric acid alone (6.8 M). After a reaction time of one hour in mixture, the total iron concentration was 24.5 g/L and after 3.25 hours, it was 27.5 g/L (98% extraction). With 38 vol% H_2SO_4 alone and a leach time of four hours, the total iron recovered was 26.5 g/L (Figure 4). The small advantage of the H_2SO_4/HCl mixture is not justified because of the higher cost of HCl.

3.1.5 Alkaline leaching of the ash

Leaching with alkalis (NaOH, $Ca(OH)_2$, and NH_4OH) was carried out in an attempt to solublize elements such as phosphorus, aluminum and zinc which are soluble in basic solutions. With sodium hydroxide concentrations from 0.1 to 10 M and leaching at 90^{0}C (194^{0}F), only a few mg/L of these metals were extracted. The maximum phosphorus extraction was about 20% and was obtained with a 10 M (400 g/L) NaOH solution.

The use of calcium hydroxide solutions ranging from 0.1 to 10 M, at 90^{0}C (194^{0}F) resulted in no phosphorus or metal extraction. This was not unexpected.

Ammonium hydroxide rapidly evaporates at 90^{0}C (194^{0}F), so leaching was carried out at 21^{0}C (70^{0}F) and 50^{0}C (122^{0}F). The ammonia concentrations used were 1, 3, and 5 M (as NH_3) with and without ammonium sulphate at 1, 3, and 5 M (as NH_3). As with the other alkalis, these reagent mixtures leached only a few mg/L of the metals and the phosphorus after four hours.

3.1.6 Effect of particle size on leaching

A sieve analysis of the ash produced at 816^{0}C (1500^{0}F), 871^{0}C (1600^{0}F) and 927^{0}C (1700^{0}F) was carried out using Tyler standard screens. The results are presented in Table 4. The particle size increased as the incineration temperature was increased.

TABLE 4. PARTICLE SIZE ANALYSIS OF INCINERATOR ASH

Particle Size Fraction (Tyler Mesh)	Weight Fraction (%)		
	Incineration Temperature		
	816^{0}C	871^{0}C	927^{0}C
+16	5.8*	24.1	41.8
+30	62.8	32.6	31.8
+60	14.9	22.4	11.1
+100	5.2	9.4	3.6
+200	4.3	6.0	4.3
-200	7.0	5.5	7.4

* % retained except for -200 which was % passing all screens.

Samples of the middle four size fractions (+30 to +200) were leached with sulphuric acid at the optimum concentration for each incineration temperature. The results for the 871^{0}C (1600^{0}F) product are presented in Figure 6.

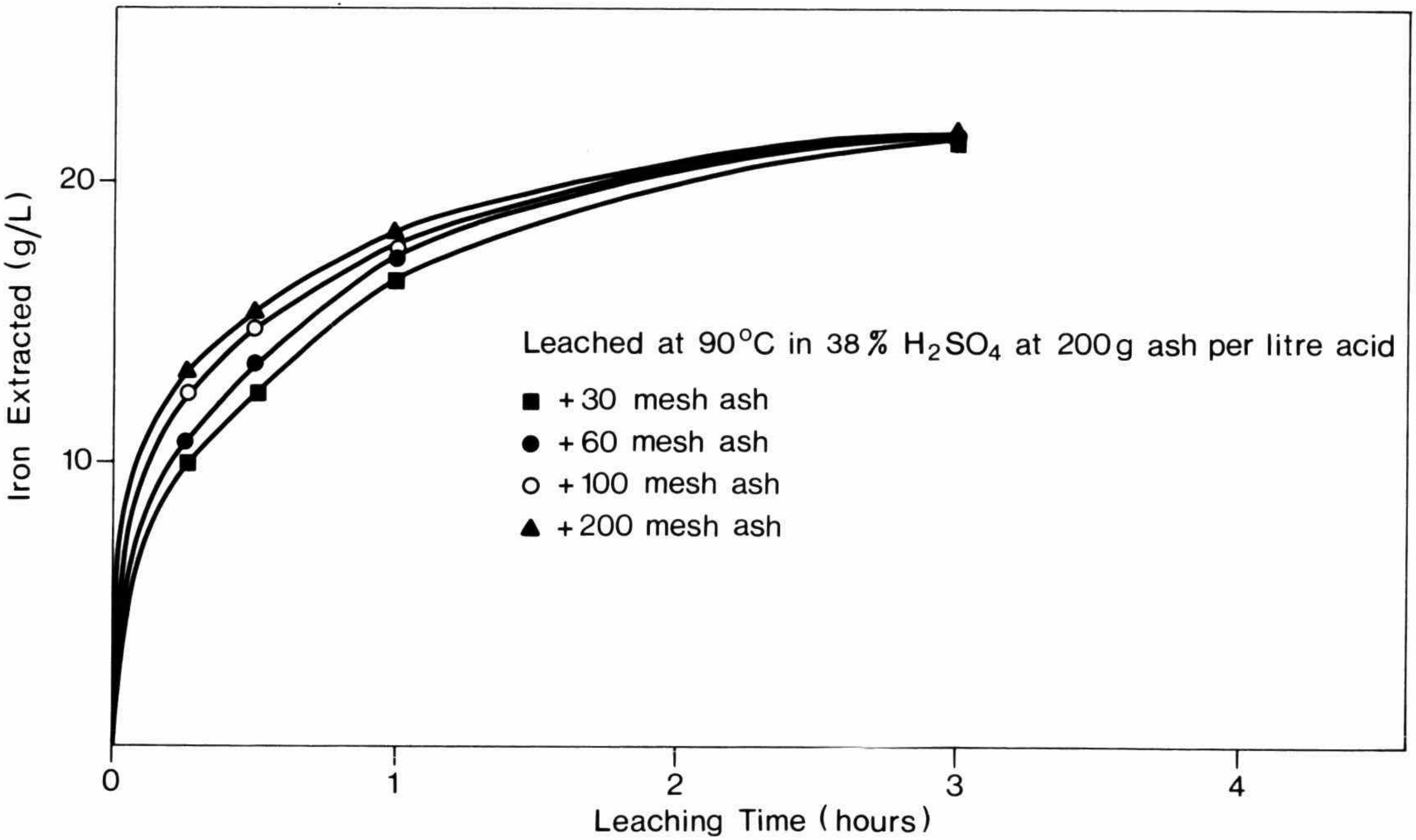

FIGURE 6 THE EFFECT OF ASH PARTICLE SIZE ON IRON EXTRACTION FROM 871°C INCINERATOR ASH.

The iron was initially dissolved more rapidly from the finer particles. However, after three hours, the concentration of iron extracted was independent of mesh size.

3.2 Iron Precipitation from Sulphuric Acid Solutions

It was established earlier (Figure 3) that above a certain acid concentration (i.e., 15 vol% for 760^{0}C ash), iron solubility in H_2SO_4 decreases.

Iron precipitation from acid extract was tested by adding concentrated H_2SO_4 to the extract. The experiments were conducted at 21^{0}C (70^{0}F) with initial iron concentrations of 21 g/L, 26 g/L and 31 g/L in the acid extract. As expected, the iron content of the solutions decreased with increased addition of concentrated sulphuric acid. The iron was precipitated as ferric sulphate. The supernatant phosphorus concentration also decreased. These solubility relations are shown in Figure 7. Linear regression analysis showed that in the concentration range 33 to 48 vol% H_2SO_4, both iron and phosphorus precipitations were inversely related to sulphuric acid concentration in the extract:

$$Fe^{3+}\ (g/L) = -1.463\ (\%\ H_2SO_4) + 75.2 \qquad r = -0.887 \qquad (1)$$

$$P\ (g/L) = -0.221\ (\%\ H_2SO_4) + 18.9 \qquad r = -0.774 \qquad (2)$$

Aluminum and nickel precipitation showed similar relationships:

$$Al^{3+}\ (g/L) = -0.0425\ (\%\ H_2SO_4) + 4.18 \qquad r = -0.950 \qquad (3)$$

$$Ni^{2+}\ (g/L) = -0.00254\ (\%\ H_2SO_4) + 0.202 \qquad r = -0.944 \qquad (4)$$

The precipitation of the above elements appears to depend only on sulphuric acid content and for a given increase in acid concentration, much more iron than the other elements will precipitate.

The copper and zinc concentrations in solution also decrease with increasing H_2SO_4 content but these metal concentrations also depend on the

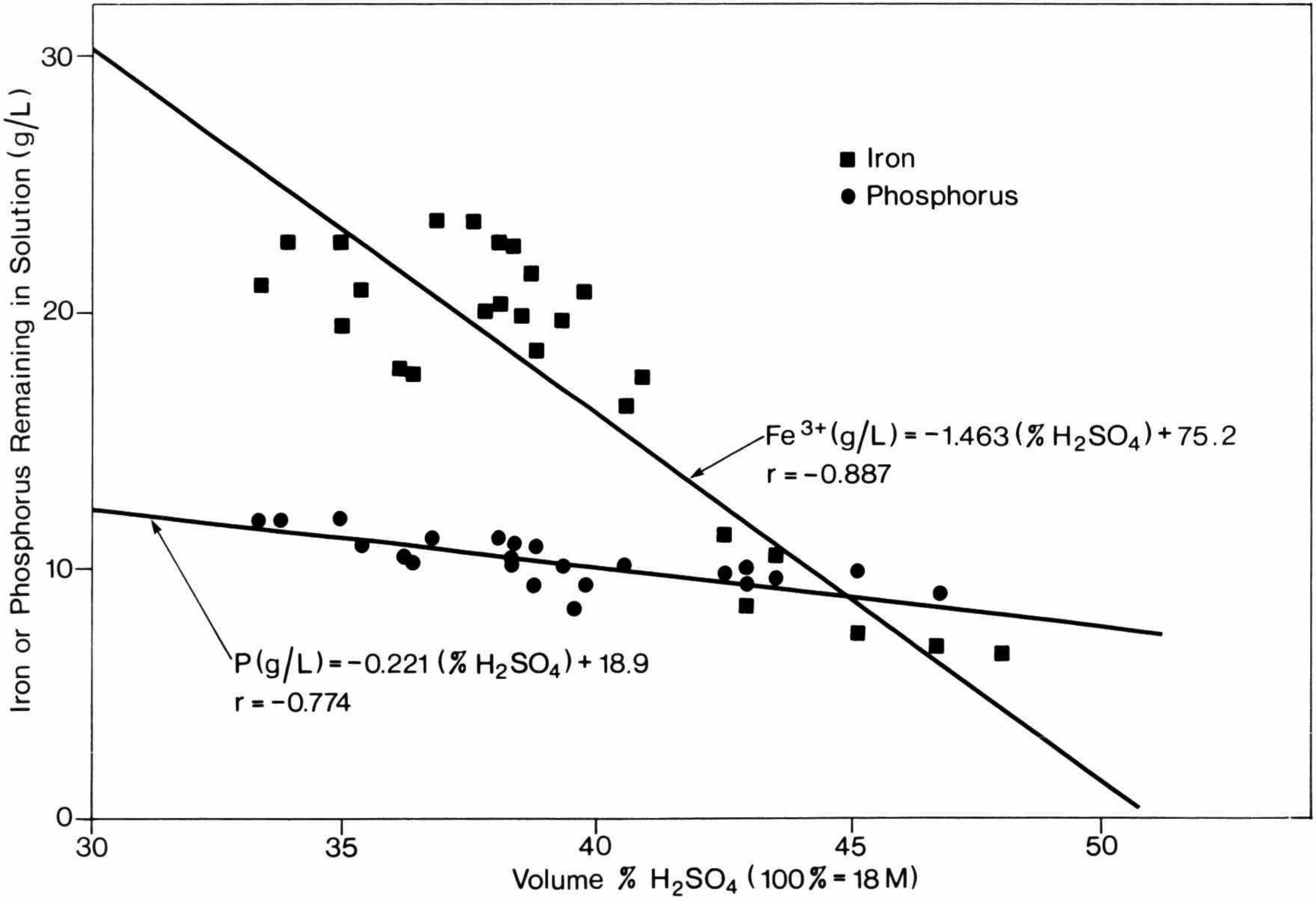

FIGURE 7 THE PRECIPITATION OF IRON AND PHOSPHORUS FROM STRONG SULPHURIC ACID SOLUTIONS.

initial iron content of the solution. These two metals appear to absorb on the surface of the iron sulphate crystals rather than precipitate with acid addition.

Typical behaviour of each of these two metal groups is shown in Figure 8 (as represented by curves for Al^{3+} and Zn^{2+} vs. vol% H_2SO_4).

In these sulphuric acid-iron precipitation experiments, at various temperatures and sulphuric acid concentrations, the dissolved iron concentration was also measured as a function of time. Nucleation and crystal growth was observed to be slow and erratic. The reaction time for crystalization varied from two to eight hours. As a result, seeding experiments were carried out.

The effect of varying amounts of added seed [wet $Fe_2(SO_4)_3$ filter cake] on the separation of iron from solution is shown in Figure 9. Seeding (i.e., precipitate recycle) appears to be desirable and necessary for the precipitation to proceed rapidly. (Note that the quantity of seed is given as Fe^{3+}. The wet filter cake was 6.2 ± 0.2% Fe^{3+} by weight.)

Figure 10 shows the effect of temperature on the precipitation rate. At the higher temperatures, precipitation proceeded more rapidly, but less completely than at the lower temperatures. The time required for equilibrium precipitation was decreased to 20 minutes when 9.0 g/L seed precipitate (as Fe^{3+}) at 73°C (163°F) was used.

The precipitation temperature should be as high as possible to minimize the reheating of the resultant acid to the leaching temperature. Temperatures in the 70 to 80°C (158 to 176°F) range appear promising as they yield soluble iron residuals in the range of 6 g/L to 7 g/L in 20 to 25 minutes. The iron remaining in solution is not lost since it would be recycled with the acid to leach new ash.

3.3 Effect of Acid Recycle on Leaching Efficiency

The effect of acid recycle was investigated by leaching fresh incinerator ash at 871°C (1600°F) with sulphuric acid recovered from the precipitation step.

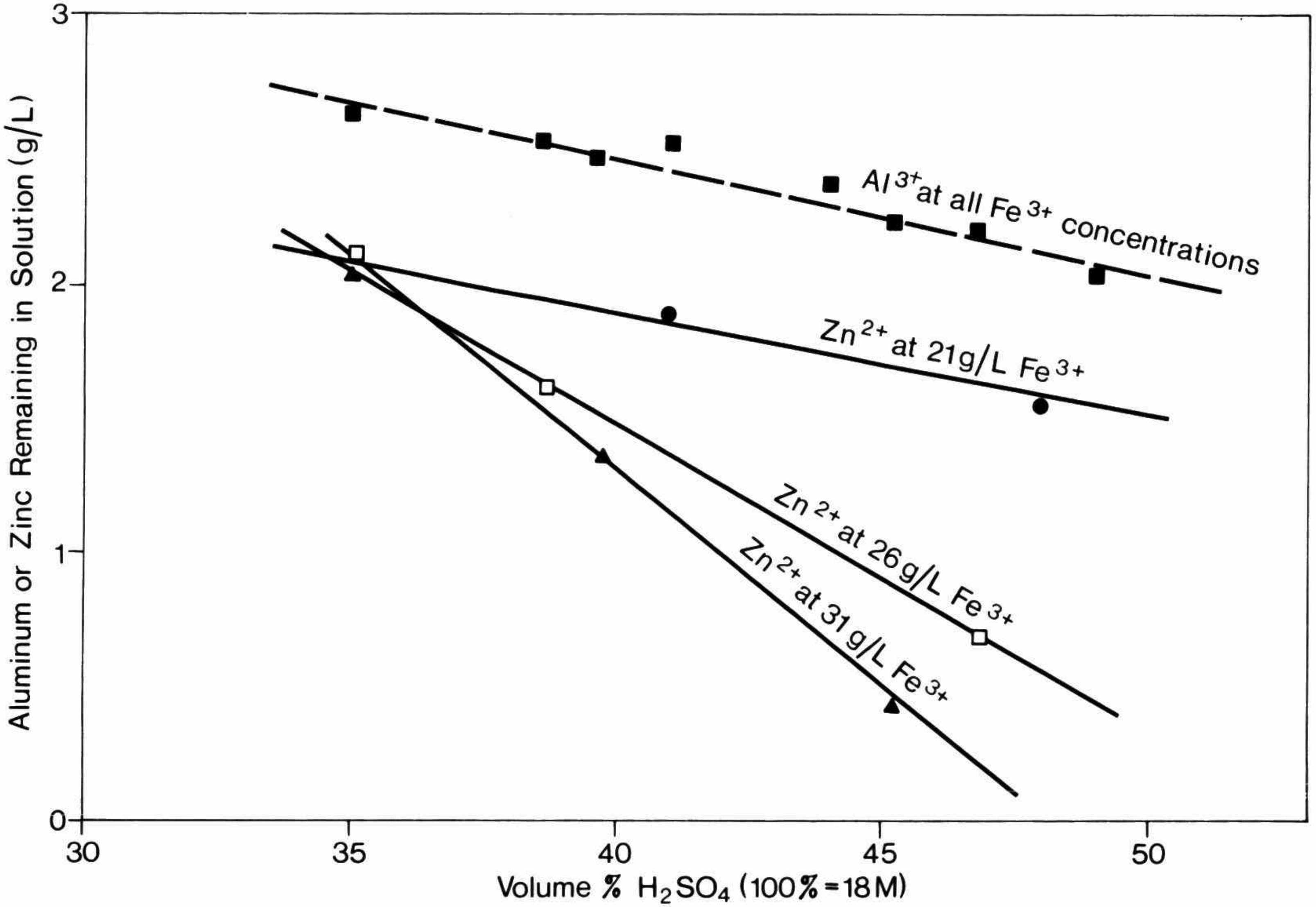

FIGURE 8 THE PRECIPITATION OF ALUMINUM AND ZINC FROM STRONG SULPHURIC ACID SOLUTIONS.

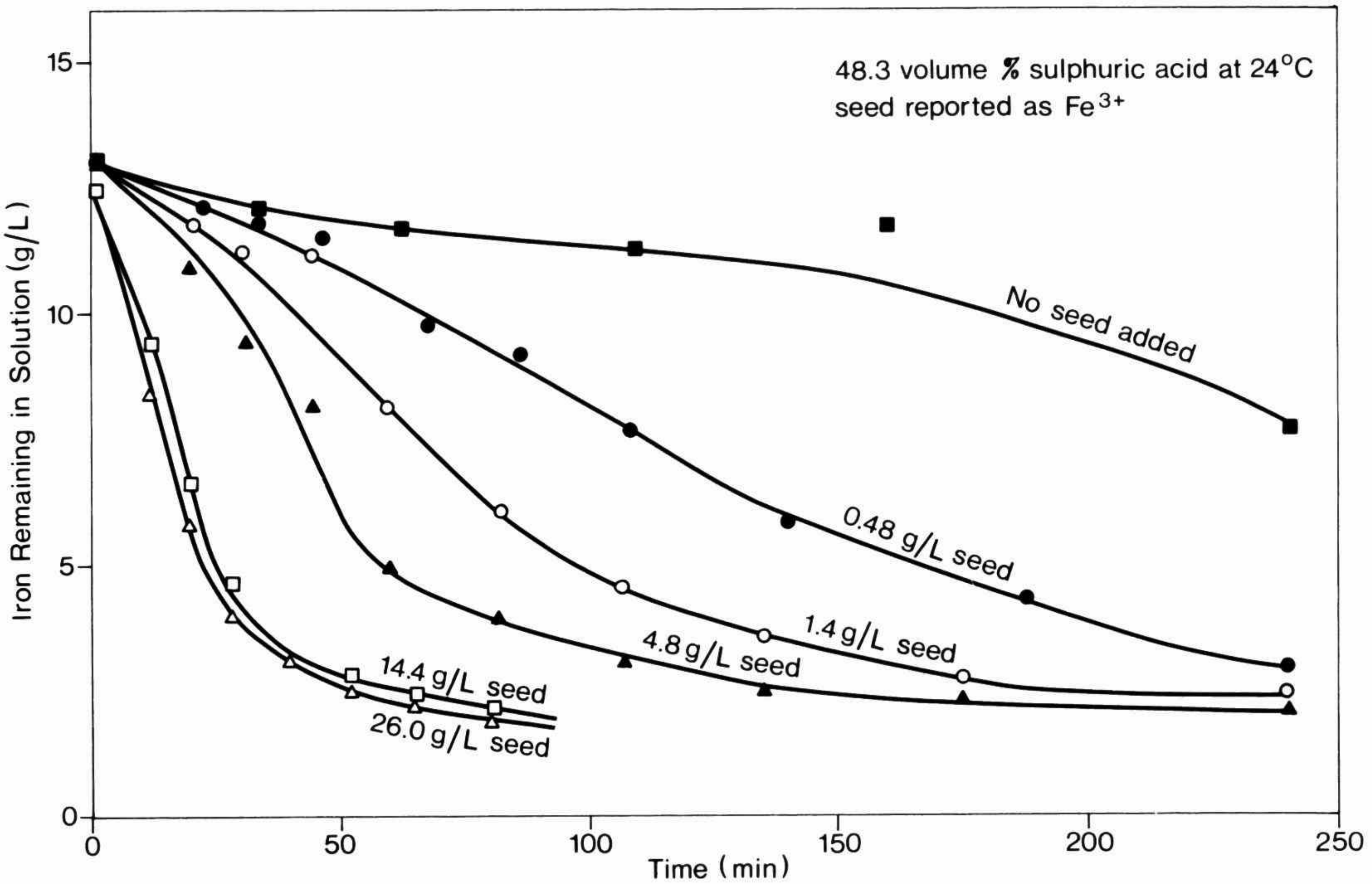

FIGURE 9 THE EFFECT OF $Fe_2(SO_4)_3$ SEEDING ON THE RATE OF IRON PRECIPITATION FROM STRONG SULPHURIC ACID SOLUTIONS.

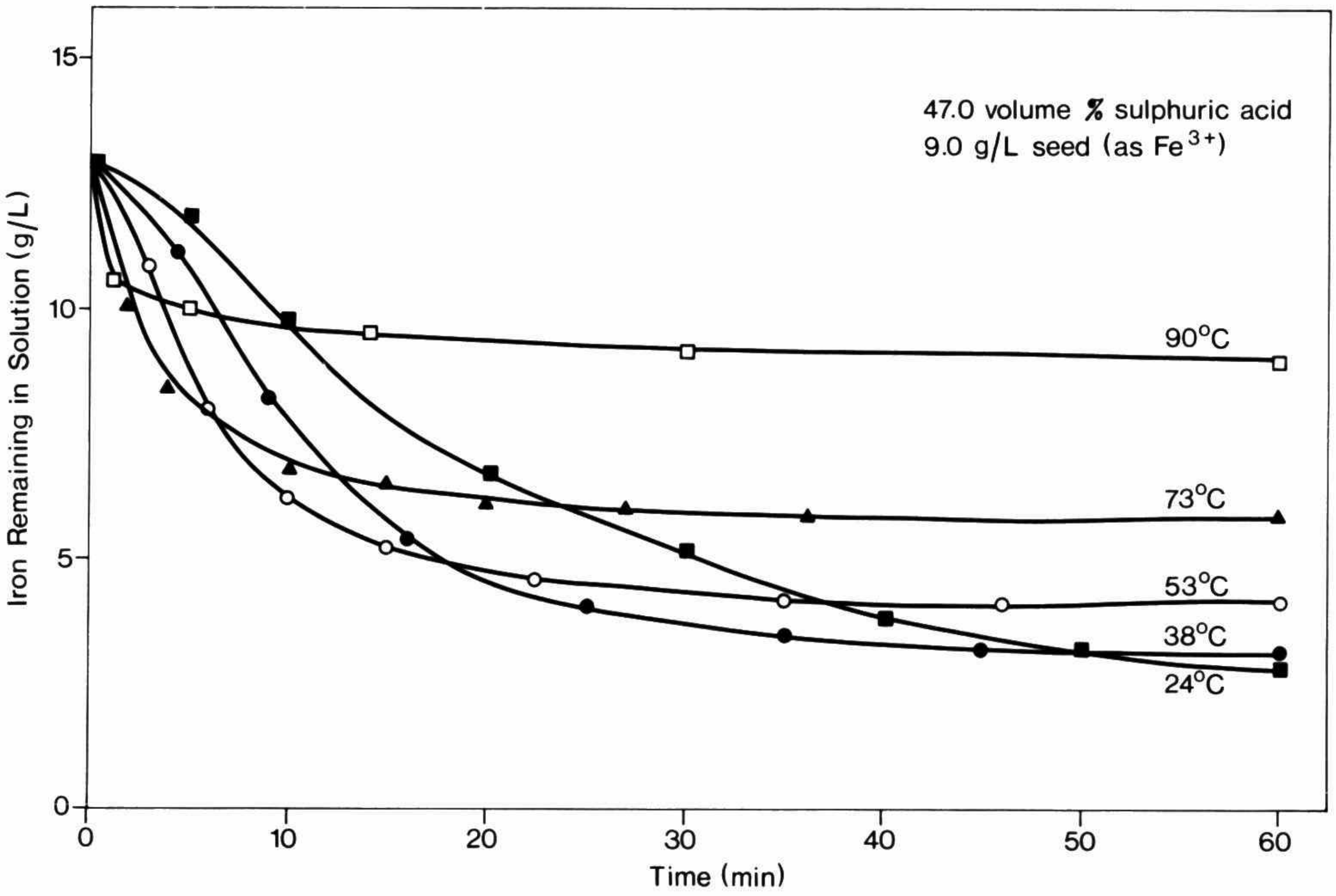

FIGURE 10 THE EFFECT OF TEMPERATURE ON THE RATE OF IRON PRECIPITATION FROM STRONG SULPHURIC ACID SOLUTIONS.

The steps in the process were:

1. slurry 200 g or 300 g of ash in 1 litre of 38 vol% (6.8 M) H_2SO_4 at 90^0C for four hours;
2. filter the slurry to separate the supernatant from the wet ash residual;
3. add sufficient concentrated H_2SO_4 to bring the acid content to 45 to 48 vol% (8.1 to 8.6 M);
4. bring to 73^0C;
5. add 161 g wet $Fe_2(SO_4)_3$ filter cake (10 g/L as Fe^{3+}) and stir for one hour;
6. filter to separate the supernatant from the $Fe_2(SO_4)_3$ precipitate;
7. dilute the recycled supernatant with water to 38 vol% H_2SO_4
8. dissolve all but 161 g of $Fe_2(SO_4)_3$ filter cake in H_2O. The remaining precipitate is used as seed in the next cycle. This is equivalent to 60% recycling of iron.

This process was repeated six times (six cycles) to determine the build-up of phosphorus and metals in the acid solutions and to examine their effect on the quality of the $Fe_2(SO_4)_3$ product. A schematic presentation of the iron extraction process is given in Figure 11. Acid losses result from:

1. chemical consumption in the dissolution of iron and other species;
2. interstitial water (acid) on the insoluble wet ash residue; and
3. interstitial water (acid) on the wet $Fe_2(SO_4)_3$ filter cake.

In these tests an average of 200 ml make-up H_2SO_4 was required per 300 g ash to balance acid losses. It was added to the acid extract (step 3) to increase the acid concentration from 31 vol% to 46 vol% to precipitate the $Fe_2(SO_4)_3$ from solution. After filtration of the $Fe_2(SO_4)_3$ precipitate, the supernatant solution was diluted with water to give the original volume of 38 vol% H_2SO_4 (6.8 M), which was then reused to leach fresh ash. When leaching at 200 g ash per litre acid, the addition of 98 vol% H_2SO_4 to balance the acid losses was smaller than in the 300 g ash case and resulted in a final acid concentration of 42.7 vol% which was insufficient to cause good $Fe_2(SO_4)_3$ precipitation.

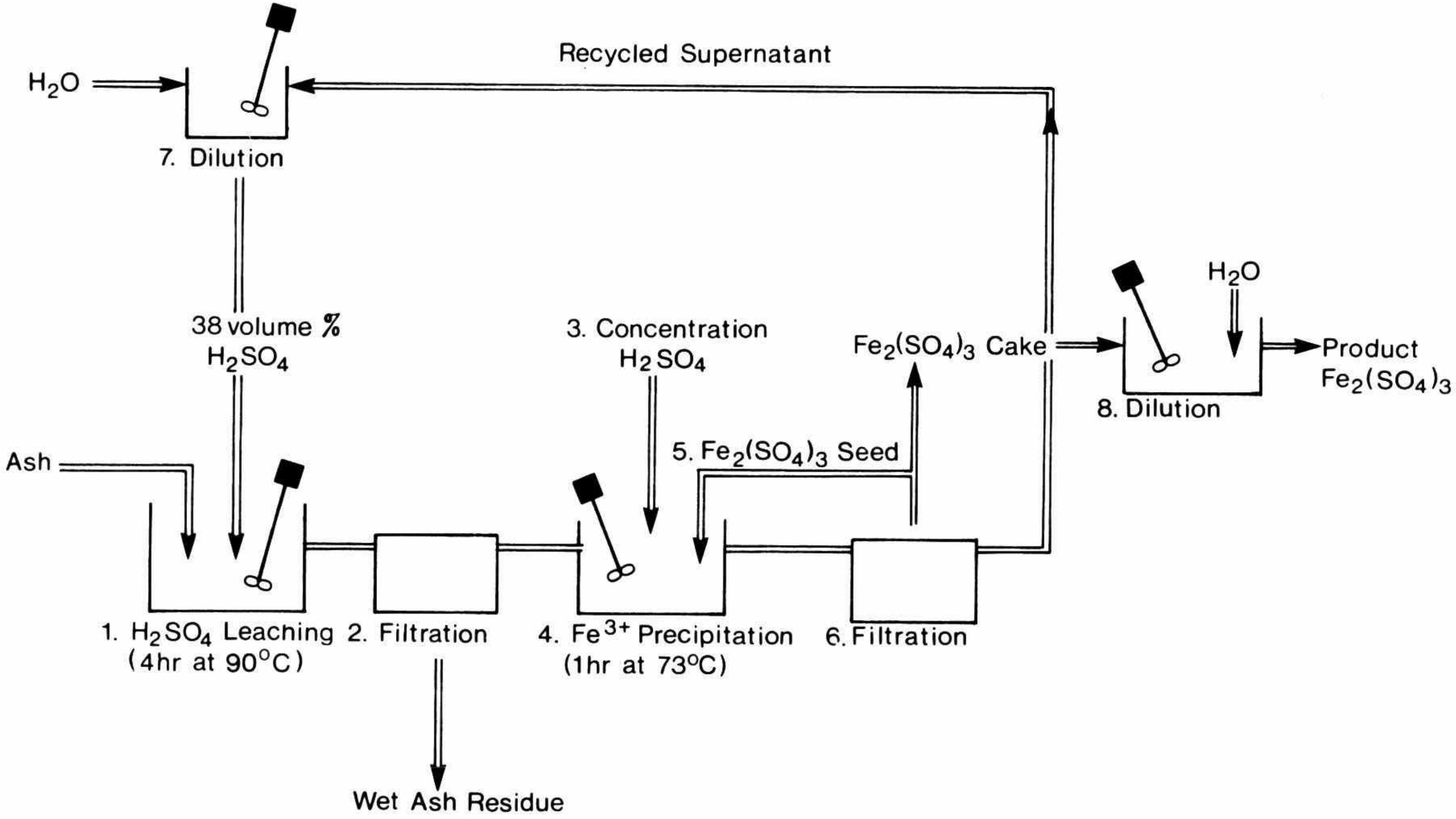
Recycled Supernatant
H_2O
7. Dilution
38 volume %
H_2SO_4
3. Concentration
H_2SO_4
$Fe_2(SO_4)_3$ Cake
H_2O
Product
$Fe_2(SO_4)_3$
8. Dilution
5. $Fe_2(SO_4)_3$ Seed
Ash
1. H_2SO_4 Leaching
(4hr at 90°C)
2. Filtration
4. Fe^{3+} Precipitation
(1hr at 73°C)
6. Filtration
Wet Ash Residue

FIGURE 11 IRON EXTRACTION PROCESS SCHEMATIC

The concentration of iron, phosphorus and sulfuric acid at various stages in the process for the six experimental cycles are presented in Table 5. The ash used in the experiment contained 8.0% iron and 5.0% phosphorus (i.e., 24 g Fe^{3+} and 15 g P per 300 g ash). It was leached with supernatant from the precipitation step diluted to 38 vol% H_2SO_4. The diluted acid contained 12.8 g/L residual Fe^{3+} and 19.0 g/L residual P. Leaching increased the iron content to 39.7 g/L Fe^{3+} (average of last three cycles), an iron extraction efficiency of 73.5%. Leaching increased the phosphorus content of the extract to 29.6 g/L P. This phosphorus extraction level was significantly lower than that obtained with virgin sulphuric acid (Table 2). When the process reached equilibrium after three to four cycles, iron was beneficiated by a factor of 2.8 with respect to phosphorus.

TABLE 5. COMPOSITION OF ASH, PRECIPITATE AND LIQUID STREAMS IN THE IRON EXTRACTION PROCESS

	Ash Composition			Acid Extract from Ash Leaching				Supernatant from $Fe_2(SO_4)_3$ Precipitation				$Fe_2(SO_4)_3$ Wet Precipitate (excluding seed for recycle)			
Cycle	Wt(kg)	Fe(%)*	P(%)*	Vol(l)	Fe^{3+}(g/L)	P(g/L)	H_2SO_4(%)**	Vol(L)	Fe^{3+}(g/L)	P(g/L)	H_2SO_4(%)**	Wt(kg)	Fe(%)*	P(%)*	H_2SO_4(%)**
1	0.300	8.0	5.0	0.725	25.8	12.6	33.2	0.775	9.0	12.2	48.4	0.173	6.41	0.70	52.1
2	0.300	8.0	5.0	0.794	31.6	18.3	31.3	0.813	16.6	17.2	45.6	0.181	6.00	0.88	49.9
3	0.300	8.0	5.0	0.704	37.7	26.7	31.6	0.741	15.6	22.0	48.0	0.226	6.13	1.05	51.5
4	0.300	8.0	5.0	0.759	38.1	28.0	31.5	0.773	15.0	21.9	46.6	0.216	6.38	1.34	52.1
5	0.300	8.0	5.0	0.763	40.2	32.3	30.8	0.817	16.1	24.5	46.7	0.249	6.12	1.27	49.5
6	0.300	8.0	5.0	0.778	40.7	28.6	31.9	0.780	17.6	25.5	45.6	0.320	6.11	1.58	50.1
Avg. of 4, 5 & 6	0.300	8.0	5.0	0.767	39.7	29.6	31.4	0.790	16.2	24.0	46.3	0.262	6.20	1.40	50.6

* weight percent
** volume percent

Table 6 shows the composition of the resultant $Fe_2(SO_4)_3$ filter cake. The values presented are an average of the final three equilibrium cycles. This filter cake was soluble in water and gave a resultant solution which contained about 35 g/L iron, 7.9 g/L phosphorus and 16.0% (2.9 M) sulfuric acid. The following Section (3.4) discusses tests with this solution for phosphorus removal from degritted raw sewage.

TABLE 6. COMPOSITION OF THE $Fe_2(SO_4)_3$ FILTER CAKE FROM LEACHING 300 g/L OF ASH

Constituent	wt% as Metal	wt% as Metal Sulfate
Al	0.42	2.82
Cr	0.07	0.26
Cu	0.05	0.13
Fe	6.2	22.1
Mn	0.04	0.11
Ni	0.01	0.02
Pb	0.001	0.001
Zn	0.27	0.71
H_2SO_4	50.6 as H_2SO_4	50.6 as H_2SO_4
H_3PO_4	1.4 as P	4.4 as H_3PO_4

3.4 Jar Testing of the Ferric Sulphate Product for Phosphorus Removal

Jar tests were conducted with the ferric sulphate precipitate and commercial ferric chloride. The average of five jar test results with each reagent is presented in Figure 12.

Influent and effluent concentrations of metals and phosphorus at the optimum iron dosage are shown in Table 7. The iron (Fe^{3+}) dosage for a 1 mg/L residual total phosphorus concentration in the effluent was 18 and 24 mg/L for $FeCl_3$ and recovered $Fe_2(SO_4)_3$, respectively. This was to be expected as 5.4 mg/L phosphorus was added along with the 24 mg/L Fe^{3+} in the recovered $Fe_2(SO_4)_3$ solution.

It should be noted that there may be a problem when precipitated ferric sulphate is used in low alkalinity wastewaters since the wastewater alkalinity may be exceeded by the excess sulfuric acid in the ferric sulfate solution and cause the pH to drop excessively. This would result in poor phosphorus removal and a high metals content in the effluent. In cases where the wastewater alkalinity is low or, for other reasons, low pH problems are encountered, neutralization with lime should be considered.

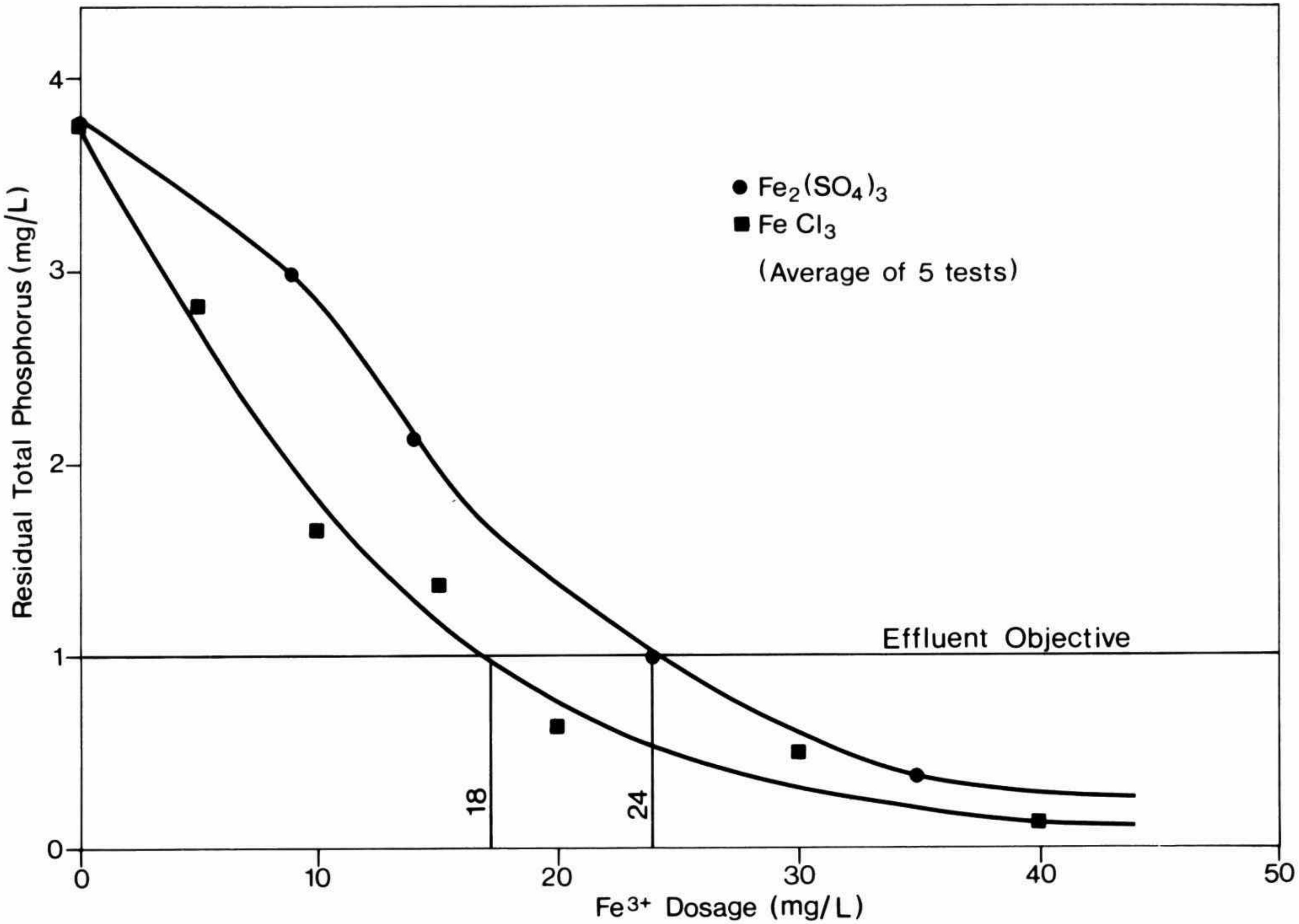

FIGURE 12 JAR TEST RESULTS COMPARING $FeCl_3$ AND RECOVERED $Fe_2(SO_4)_3$ FOR PHOSPHORUS REMOVAL.

TABLE 7. EXPECTED METAL AND PHOSPHORUS LOADINGS IN THE INFLUENTS AND EFFLUENTS OF A PRIMARY PHOSPHORUS REMOVAL PROCESS BASED ON JAR TESTS*

Parameter	Influent						Effluent	
	$FeCl_3$ (18 mg/L as Fe^{3+})			$Fe_2(SO_4)_3$ (24 mg/L as Fe^{3+})			$FeCl_3$	$Fe_2(SO_4)_3$
	Background	Due to $FeCl_3$	Total	Background	Due to $Fe_2(SO_4)_3$	Total		
Al	0.15	0.004	0.15	0.12	1.9	2.0	0.07	0.30
Cr	0.02	0.007	0.03	0.02	0.29	0.31	0.02	0.02
Cu	0.083	0.003	0.086	0.064	0.19	0.25	0.25	0.03
Fe	0.90	17.6	18.5	0.53	24.1	24.6	1.1	2.4
Mn	0.083	0.091	0.174	0.084	0.16	0.24	0.15	0.20
Ni	0.021	0.015	0.036	0.015	0.036	0.05	0.052	0.083
Zn	0.31	0.024	0.33	0.25	1.06	1.31	0.20	0.75
P	3.6	0	3.6	3.8	5.4	9.2	1.0	1.0
pH	7.5			7.5			7.1	6.2

* All elements expressed as mg/L except pH.

3.5 Preliminary Cost Evaluation of the Iron Recovery Process

The steps involved in the iron recovery process were discussed in Section 3.3. Obviously, a large portion of the process cost will be for H_2SO_4. As a first examination of process economics, a cost estimate based on acid requirements only was prepared for the Hamilton sewage treatment plant (60 MIGD; 90,000 lb/day ash). This estimate is shown in Appendix A.

Cost reduction may result from more efficient sulfuric acid usage (i.e., better recovery for each step) or by using a source of acid which is cheaper; (e.g., an industrial by-product). Phosphorus recovery may also help offset costs. Diosady (1974) found that a distillation process could recover phosphoric acid and break even.

However, when the cost of concentrated H_2SO_4 required to recover Fe^{3+} [121¢/kg Fe^{3+} (56¢/lb Fe^{3+})] is compared to the commercial ferric chloride cost of 53¢/kg Fe^{3+} (24¢/lb Fe^{3+}), iron recovery from incinerator ash may be seen to be uneconomical at this time, in the Toronto-Hamilton area.

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APPENDIX

ESTIMATE OF H_2SO_4 COST FOR $Fe_2(SO_4)_3$ RECOVERY

From Section 3.3:

1) Processing 300 g ash required 200 ml makeup H_2SO_4.

2) Processing 300 g ash produced 262 g filter cake (6.2% Fe^{3+}).

In terms of pounds of ash processed:

$$200 \text{ ml} \times \frac{1 \text{ L}}{1000 \text{ ml}} \times \frac{1 \text{ gal}}{4.54 \text{ L}} = 0.0441 \text{ gal acid}$$

$$300 \text{ g} \times \frac{1 \text{ lb}}{454 \text{ g}} = 0.66 \text{ lb ash}$$

$$\frac{200 \text{ ml}}{300 \text{ g}} = \frac{0.0441 \text{ gal}}{0.66 \text{ lb}} = 0.0667 \text{ gal/lb ash}$$

1) Processing 1 lb of ash requires 0.0667 gal makeup H_2SO_4.

0.66 lb ash produces $0.66 \times \frac{262}{300} = 0.576$ lb cake.

1 lb ash produces 0.576 lb/0.66 = 0.873 lb cake.

The cake is 6.2% Fe^{3+}.

2) Processing 1 lb of ash produces 0.873 x 0.062 = 0.054 lb Fe^{3+}.

Therefore, 0.0667 gal of conc. H_2SO_4 are required to produce 0.054 lb Fe^{3+},

or Producing 1 lb of Fe^{3+} requires 1.235 gal of conc. H_2SO_4.

Conc. H_2SO_4 costs 45¢/gal (in bulk tank trucks)*

Cost of H_2SO_4 to produce 1 lb of Fe^{3+} by the proposed extraction process is 1.235 gal x 45¢/gal = 56¢/lb of Fe^{3+}.

Cost of commercial $FeCl_3$ for phosphorus removal is 24¢/lb of Fe^{3+}**.

Note: 1 lb = 454 g.
1 gal = 4.54 litres.

* FOB Toronto - Hamilton area, October 1977 from McArthur Chemical Company, Toronto.

** FOB Toronto - Hamilton area, October 1977 from Diversey Chemical Company, Clarkson.

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